

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
Advanced GCE

CHEMISTRY

Chains, Rings and Spectroscopy

Thursday **24 JUNE 2004**

Afternoon

1 hour 30 minutes

Candidates answer on the question paper.

Additional materials:

Data Sheet for Chemistry

Scientific calculator



2814

Candidate
Name

Centre
Number

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Candidate
Number

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TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name, Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.

DO NOT ANSWER IN PENCIL. DO NOT WRITE IN THE BARCODE. DO NOT WRITE IN THE GREY AREAS BETWEEN THE PAGES.

- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

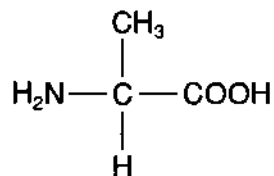
FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	11	
2	16	
3	6	
4	15	
5	17	
6	7	
7	18	
TOTAL	90	

This question paper consists of 16 printed pages.

Answer **all** the questions.

For
Examiner's
Use

- 1 Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, is an α -amino acid that is found in human sweat. Its structure is shown below.



alanine

- (a) Alanine reacts with an aqueous alkali such as sodium hydroxide to give a salt and another product.

- (i) Name the functional group in alanine which reacts with aqueous alkali.

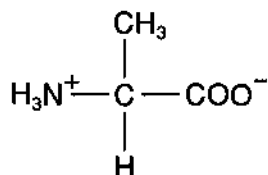
.....[1]

- (ii) Give the formula of the salt formed in the reaction of alanine with aqueous sodium hydroxide.

[2]

- (iii) What is the other product of this reaction? [1]

- (b) In sweat, alanine exists as a zwitterion. The structure of this zwitterion is shown below.

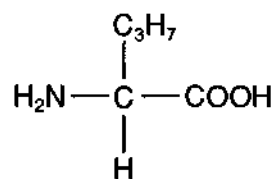


Show the structure that results when this zwitterion comes into contact with an alkali.

[2]

- (c) Human sweat also contains dipeptides in which alanine is combined with one other α -amino acid such as valine. The structure of valine is shown below

For
Examiner's
Use



valine

Explain how α -amino acids combine to give dipeptides.

Include in your answer the displayed formulae of **two** different dipeptides that can be made from alanine and valine.

.....

.....

.....

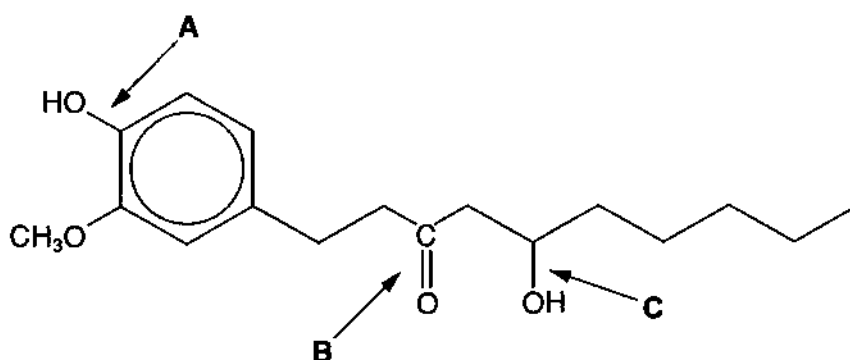
.....

[5]

[Total: 11]

- 2 Gingerol is a compound extracted from root ginger. It has a distinctive smell and creates a hot taste when put into the mouth. The structure of gingerol is shown below.

For
Examiner's
Use



gingerol

- (a) Name the **three** functional groups in gingerol labelled **A**, **B** and **C**.

A

B

C

[3]

- (b) A solution of 2,4-dinitrophenylhydrazine can be used as a chemical test to identify one of these functional groups.

- (i) Which of the functional groups, **A**, **B** or **C**, does this test identify?

.....[1]

- (ii) State what you would expect to see when gingerol was added to this test solution.

.....[2]

- (iii) State whether or not gingerol would react with Tollens' Reagent (ammoniacal silver nitrate). Explain your reasoning.

.....

.....[1]

- (c) Gingerol is thought to be produced by the plant to help protect it against attack from micro-organisms such as bacteria.

Suggest which part of the molecule is most likely to be responsible for the anti-bacterial properties.

.....[1]

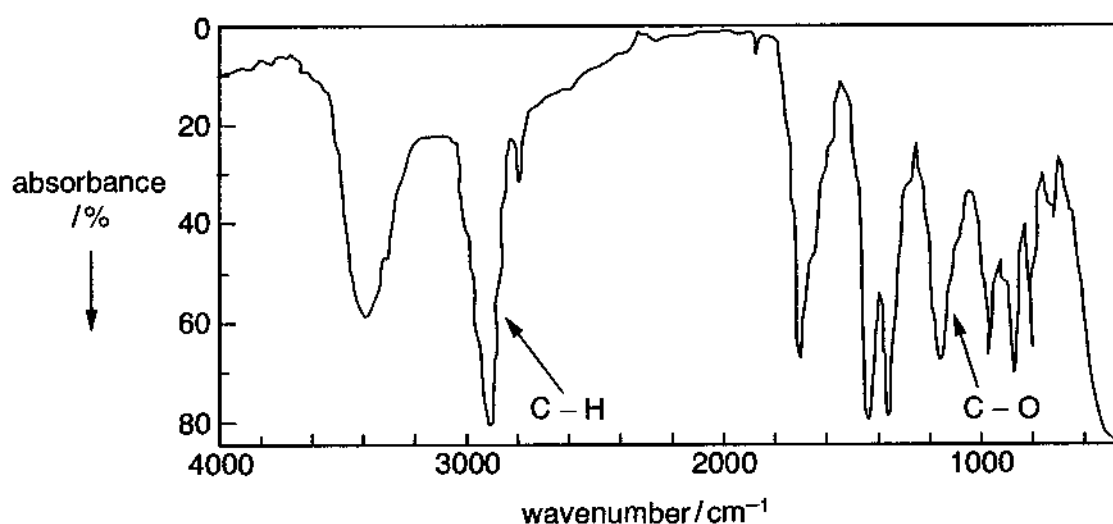
(d) Gingerol reacts rapidly with bromine.

- (i) Assuming the $\text{CH}_3\text{O}-$ group has no reaction, suggest a structure for the organic product of this reaction.

[2]

- (ii) Identify the other molecule produced in this reaction[1]

(e) An infra-red spectrum of a sample containing gingerol is shown below.



Two of the peaks have already been labelled to show the bonds responsible for the absorption.

On the spectrum, label the absorption peaks produced by **two other** bonds in the gingerol molecule. [2]

(f) Gingerol has two stereoisomers.

- (i) Explain what is meant by the term *stereoisomerism*.

.....

[2]

- (ii) Name the type of stereoisomerism shown by gingerol.

.....[1]

[Total: 16]
 [Turn over]

3 An ester, **D**, is used as a solvent for paints and varnishes.

(a) Ester **D** can be manufactured by heating an alcohol under reflux with ethanoic acid and a catalyst.

(i) State a suitable catalyst for this reaction.

.....[1]

(ii) Explain why the reaction is carried out under reflux.

.....
.....[1]

(b) Ester **D** has a structural formula, $\text{CH}_3\text{COOCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$.

(i) Draw the displayed formula of ester **D**.

[2]

(ii) State the name of the alcohol used to make ester **D**.

.....[1]

(c) Apart from being a good solvent, suggest another use for ester **D**.

.....[1]

[Total: 6]

4 In 1893, a chemist discovered an organic acid which became known as *Feist's Acid*.

For
Examiner's
Use

- (a) *Feist's Acid* contains carbon, hydrogen and oxygen only. It was found by combustion analysis to contain 50.7% carbon and 4.2% hydrogen.

Show how the information from combustion analysis can be used to calculate the **empirical formula** of *Feist's Acid*.

empirical formula [3]

- (b) Molecular mass determination was not particularly accurate in 1893, but the M_r of *Feist's Acid* was estimated to be between 138 and 144.

- (i) Show how the empirical formula you have calculated in part (a) and the approximate molecular mass can be used to deduce that the **molecular formula** for *Feist's Acid* is $C_6H_6O_4$.

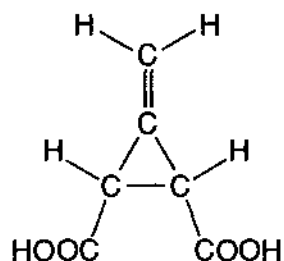
[2]

- (ii) Which method is now used for accurate determination of molecular masses?

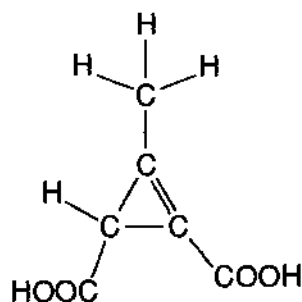
.....[1]

- (c) A number of structural isomers for *Feist's Acid* were suggested, including the two shown below.

For
Examiner's
Use



structure E



structure F

In the box below, draw **one other** structural isomer that fits the formula of $C_6H_6O_4$.



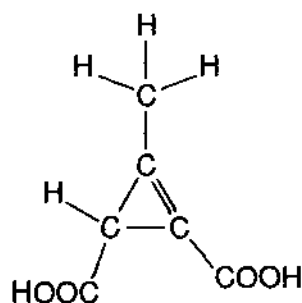
[1]

- (d) *Feist's Acid* was known to be chiral. Structure E and structure F are both chiral.

- (i) What structural feature gives rise to a chiral centre in an organic molecule?

.....
[1]

- (ii) Show by means of an asterisk * the chiral centre on this diagram of structure F.

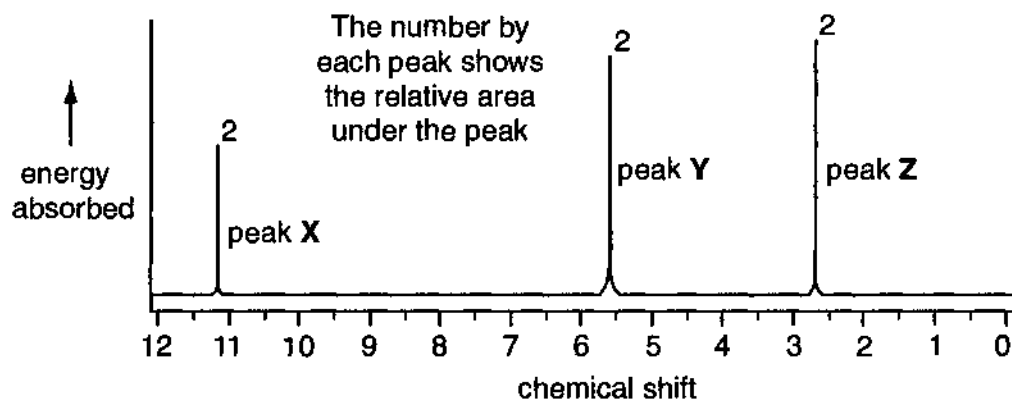


[1]

- (e) Uncertainty about the structure of *Feist's Acid* continued until the 1950s, when n.m.r. was developed.

For
Examiner's
Use

The n.m.r. spectrum of *Feist's Acid* is shown below.



- (i) Identify the type of protons responsible for peak X.

.....[1]

- (ii) Explain how D_2O can be used to help confirm which protons are responsible for peak X.

.....

[2]

- (iii) Use peaks Y and Z to decide whether structure E or structure F is correct for *Feist's Acid*.

Explain your reasoning and state how the n.m.r. spectrum for the other structure would differ.

.....

[3]

[Total: 15]

- 5 Lactic acid (2-hydroxypropanoic acid) is being used to develop biodegradable polymers for packaging material.

For
Examiner's
Use

- (a) Lactic acid can be made in the laboratory by a two-stage synthesis starting from ethanal, CH_3CHO . The first stage adds an additional carbon atom to the molecule.

For each of the two stages, write the reagents, conditions, type of reaction and a balanced equation.

stage 1 reagents

conditions

type of reaction

balanced equation

stage 2 reagents

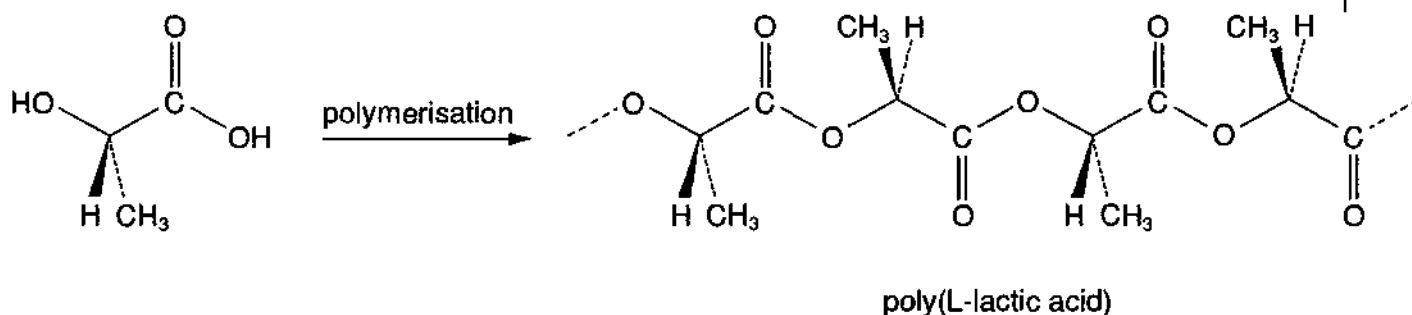
conditions

type of reaction

balanced equation

[8]

- (b) Polymerisation of the optical isomer L-lactic acid gives poly(L-lactic acid) as shown below.



- (i) State the type of polymerisation occurring in this reaction.

.....[1]

- (ii) Draw a circle around a repeat unit of the polymer section shown above. [1]

- (iii) Lactic acid can be made naturally by fermentation or synthetically as in part (a).

Suggest which of these two methods would be the most suitable source of the optical isomer L-lactic acid. Explain your answer.

.....

.....

.....[2]

(c) Poly(L-lactic acid) is a rigid polymer because of the regular arrangement of side chains. This is similar to the way rigidity can be controlled in polyalkenes.

(i) Name a hydrocarbon polymer in which the rigidity is controlled by the arrangement of the side chains along its length.

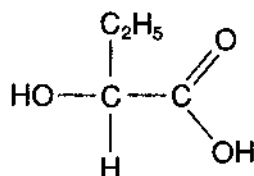
.....[1]

(ii) State the terms used to describe such a polymer with

a random arrangement of the side-chains

a regular alternating arrangement of the side-chains.[2]

(d) To produce biodegradable polymers with a greater variety of properties, polymer scientists are researching into other monomers similar to lactic acid. One example is 2-hydroxybutanoic acid shown below.



Draw a displayed or skeletal formula to show the repeat unit of poly(2-hydroxybutanoic acid).

[2]

[Total: 17]

6 Primary amines such as ethylamine and phenylamine can act as bases.

(a) Show how ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, acts as a base.

For
Examiner's
Use

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.....[4]

(b) Describe and explain the effect on the basicity when the primary amine group is attached to a benzene ring, using phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, as an example.

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.....[3]

[Total: 7]

7 Bromine will react with benzene in the presence of a catalyst.

(a) (i) Give the name or formula of a suitable catalyst for this reaction.

.....[1]

(ii) State the general name of this type of catalyst.

.....[1]

(iii) Write a balanced equation for this reaction.

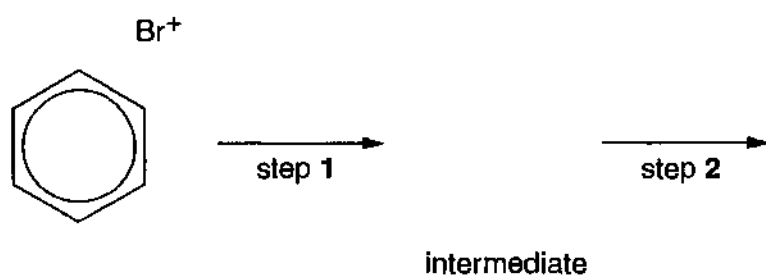
[2]

(iv) State the name of the organic product.[1]

(b) The reaction between bromine and benzene is electrophilic substitution.

Complete the scheme below to show the likely mechanism for this reaction. Assume that the electrophile is Br^+ . (You do **not** need to show the action of the catalyst.)

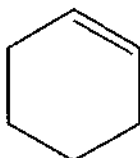
Show clearly all the curly arrows as well as the structures of the intermediate and the products.



[4]

- (c) In this question, two marks are available for the quality of written communication.

Bromine reacts much more readily with cyclohexene than it does with benzene. The reaction with cyclohexene does **not** need a catalyst. The structure of cyclohexene is shown below.



cyclohexene

- (i) Describe with the aid of diagrams the π -bonding in cyclohexene and benzene.
- (ii) Use your answer to explain why bromine reacts much more readily with cyclohexene than it does with benzene. [7]

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For
Examiner's
Use